

INFRARED INVESTIGATION OF SOME
SUBSTITUTED AMMONIUM COMPOUNDS

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CHAPTER I

INTRODUCTION

The use of infrared spectra as a possible tool in chemical research has come about only in the last twenty-five years. Previous to 1930, spectra were used chiefly in theoretical physics in the study of vibration and rotation of simple molecules. In the first decade of the century, W. W. Coblentz⁽¹⁾ had shown empirically that there was a relation between functional groups and molecular structure and infrared absorption, but due to the difficulty of detecting and measuring the radiation, its use in chemical research had not been considered. The period beginning in 1930 saw the development of methods of detecting and amplifying small electrical signals which led to the construction of several infrared spectrophotometers in this country. The war gave this field a major impulse when it was discovered that infrared spectra furnished a quick and reliable method of analyzing C_4 hydrocarbons in the production of synthetic rubber. This led to an improvement in instrumentation and the commercial production of spectrophotometers.

Most of the early work in infrared spectroscopy was done with liquids and gases. There were several reasons for this emphasis. The simple compounds which were first studied were usually either liquids or gases. In addition, the problem of sample technique in the use of liquids and gases was fairly simple, but with solids it was much more complex. Many methods have been developed for solids, none of which is completely satisfactory. The principal methods and their advantages and disadvantages are discussed below.

The Solution Method.--This method consists simply of dissolving the sample in a suitable solvent and obtaining the spectrum of the solution. Sample preparation is quick and simple, in most cases, and concentrations are readily controlled. In addition, this method sometimes increases the sharpness of bands because of the absence of association effects present in the solid. However, there are several disadvantages. The two principal ones can be considered together: the choice of solvent and the solvent absorption. The ideal solvent would dissolve everything and would absorb in the infrared not at all. Unfortunately, the least absorbing solvents have a limited solvent action, while the better solvents usually have a fairly complex infrared spectrum. Hence it is necessary to strike a balance between the two.

After a suitable solvent has been chosen there are several ways in which to overcome partially the solvent absorption. The solvent spectrum and the solution spectrum can be compared directly, and the solvent absorption subtracted to obtain the solute absorption. If a double-beam instrument is available, the spectrum can be automatically compensated for the solvent by using an equivalent amount of solvent in the reference beam. For quantitative work, where perhaps only one absorption peak is used, an empirical calibration curve will compensate for any errors produced by solvent absorption. If a reference spectrum is desired this method should not be used unless no other method is applicable. Besides the difficulty of obtaining an accurate point-by-point compensation for the solvent, the interaction of the solvent and the solute often gives rise to shifts of intensity and position of absorption peaks in the spectra of the solute and the solvent.

The Mulling Technique.---The mulling technique consists of mixing the finely divided sample with some substance, such as mineral oil or perfluorokerosene, which has a relatively simple infrared spectrum. The resulting paste is then spread on a salt plate and the spectrum obtained. This has been the most widely used method for solids for many years. The absorption of the

mulling agent can be minimized by a suitable choice. The two mentioned above can be used to cover a wide range in the infrared. Sample preparation for qualitative work is relatively simple. The method can be used on substances for which no other method is satisfactory. One disadvantage is the absorption of the mulling agent, although this is not as important as in solution spectra. The types of substances which can be used in this method are limited to those which can be ground to a fine powder. This eliminates soft materials or those which become sticky or which stretch easily. Deliquescent materials also present difficulties, but the use of low temperatures and low-humidity atmospheres will sometimes overcome this difficulty. Accurate quantitative work is almost impossible with this method. An internal standard can be used, but this is a long and tedious process. This method may give some trouble with light-scattering, but use of a small particle size (three microns or less) and the small difference in refractive indices of the sample and the mulling agent minimizes this trouble. The correct film thickness for a suitable spectrum requires an artistic approach rather than a scientific one, but with practice it presents few difficulties.

The Powder Film Technique.--The sample is milled with some volatile mulling agent and then spread on a salt

plate. The solvent is allowed to evaporate and a spectrum can be obtained from the resulting powder film. The sample preparation is tedious and sometimes involved. The mulling agent must volatilize completely or its absorption may interfere. Particle size must be maintained below 1-3 microns in order to minimize light-scattering. The advantages and disadvantages are the same as in the mulling technique except for the absence of mulling agent spectra and the greater possibility of light-scattering.

Melted Film Technique.--In this method, the sample is melted and spread on a salt plate. When it solidifies a spectrum is obtained. Alternately, the finely ground sample can be melted directly on the salt plate. The main advantage of this method is the complete absence of interference from solvents or mulling agents. A pure spectrum is obtained, but there are several disadvantages. The method is limited to those substances which can be melted easily without either decomposing, oxidizing, or polymerizing at the temperature required. This severely limits the choice of substances for which this method is applicable. Oxidation can be minimized by melting the sample in an inert atmosphere or between salt plates. One difficulty which may occur is that the sample may crystallize in a regular orientation. This often leads to the appearance or disappearance of some bands or the shifting of others

depending upon the orientation achieved. This difficulty is not apparent in the mulling or powder film techniques because of the random orientation obtained by the substance in those techniques.

The Mechanical Film Technique.---This method consists of preparing a thin film by means of a microtome or a rubber mill. The thickness of the films can be controlled easily. The spectra obtained are pure spectra free from interference from solvents or mulling agents. However, the number of compounds to which this method can be applied is limited.

The Film from Solution Technique.---This method consists of dissolving the compound in a volatile solvent and allowing the solvent to evaporate, leaving a thin film of the compound behind. The film may be cast directly on a salt plate or on mercury, a metal plate, or some other flat surface. The latter methods have the advantage of allowing the spectrum to be run without the interference fringes which sometimes occur when a salt plate is used. The film is simply lifted off of the surface and the spectrum obtained. The main problem in the use of this technique is the choice of solvents. The solvent must satisfy several requirements. It must dissolve an appreciable amount of the compound at a moderate temperature. It must not react with the compound. It must not

leave any non-volatile matter behind upon evaporation. It must deposit a clear and even film of the compound. The method of evaporation often plays an important part; for one compound, a slow evaporation followed by vacuum treatment will produce a good film, while another compound may require fast evaporation at an elevated temperature in order to obtain the desired film. Once a good procedure has been found this method has distinct advantages, but the discovery of such a procedure will often entail a great deal of preliminary work. If a large variety of compounds are to be used, a different technique may be needed for each one.

The Pressed Medium Technique.--There are two principal methods using a pressed medium for obtaining the spectrum of a solid. In the first, the sample is placed between sheets of some substance such as silver chloride, mica, or polyethylene and then rolled and milled to obtain a "sandwich" of the compound in which the sample has been rolled into a thin, clear film. The rolling and milling may be done at elevated temperatures if necessary. Since a known amount of sample can be used, this method may be used for quantitative work. Compounds which are not plastic enough to be rolled can be ground into a fine powder and then rolled between polyethylene sheets until the polyethylene is impregnated with the

particles. The main objection to this method is the presence of absorption bands due to the materials used as carriers. This method was first proposed by Sands and Turner. (2)

In the second method using a pressed medium, the finely ground sample is mixed with finely ground potassium bromide and the mixture placed in a special die where it is subjected to high pressure under a vacuum. The result of this treatment is a clear plate of potassium bromide with the sample imbedded in it. The spectra obtained by this method are pure spectra because the potassium bromide is transparent throughout the rock salt region of the spectrum. Since a known weight of the compound and potassium bromide can be used, quantitative work is possible. The sample preparation is not difficult once the proper proportions of sample and potassium bromide are chosen. This method is limited to those compounds which can be ground to the necessary size.

Special Techniques.--In cases where none of the above methods is applicable, it is possible to obtain the spectra of the decomposition products of the compound and obtain some information about its structure. Comparison with the decomposition products of similar materials may also be useful. This method, however, is used only as a last resort, since for most compounds, one of the previous methods will be applicable.

The above-mentioned techniques include all of the common methods for obtaining the infrared spectrum of a solid substance. One or more of the methods are usually applicable to a given problem. The choice of method, if a choice is available, will depend upon the type of work which is to be done. For example, an analytical problem will probably not require a pure reference spectrum, since only a few bands are needed. On the other hand, a structure problem will probably require a good reference spectrum.

In the present problem, the compounds studied are all substituted ammonium salts. A single method was sought which would be applicable to all of the compounds. The method chosen was the pressed potassium bromide technique. This and the mulling technique are the only methods which are easily applicable to all of the compounds studied. The mulling technique was not used because of the interference from the mulling agent spectrum.

The pressed potassium bromide technique has been used for only a short time. It was first proposed by Sister Stimson in 1951.⁽³⁾ Much of the work on the development of the techniques was done by Schiedt⁽⁴⁾ who investigated the use of salts other than potassium bromide and the conditions needed to produce a clear plate. This method is rapidly replacing the mulling technique in most laboratories because of the ease of sample preparation and the application to quantitative work.

The principal purpose of the present study was to investigate the infrared spectra of the NH_3^+ , NH_2^+ , and NH^+ groups. These groups are very similar to the methyl, methylene and tertiary CH groups which have been thoroughly studied, particularly by the oil industry. However, these nitrogenous analogues have not been investigated to any great extent. Most of the work on these groups has been done in connection with the biologically important amino acids. Edsall's early work on the Raman spectra^(5,6) showed that amino acids existed in the zwitterion form almost exclusively. Since then, several groups of workers⁽⁷⁻¹⁰⁾ have studied amino acids and their hydrochlorides and have defined a number of correlations. A number of these correlations involve the NH_3^+ group which is present in many amino acids. To a certain extent, the NH_2^+ group has been studied also, since some amino acids contain this group. However, in none of the works cited has a reasonably complete assignment been made of the vibrations which would be expected from these groups, nor has the effect of these groups on neighboring groups been determined.

Since most of the compounds studied were rather complex, a completely theoretical approach was not possible. The methyl ammonium ion is the simplest compound studied and might lend itself to a theoretical study. Such a

study has been published by Waldron,⁽¹¹⁾ who studied single crystals of methyl ammonium chloride. In this study, however, an empirical approach was used with the few theoretical studies available used as guides.

CHAPTER II

EXPERIMENTAL TECHNIQUES

Preparation of Compounds

All of the alkyl ammonium salts in this study were prepared by a method described by Childers.⁽¹²⁾ This consists of treating the amine with an approximately equivalent amount of 48% HBr in the cold. After the reaction has taken place, the solution is carefully neutralized with either the amine or with a strong sodium hydroxide solution. The neutral solution is then heated on a water bath until most of the water and excess amine have been driven off. The solution is then cooled in an ice bath. If the salt does not precipitate out, it is brought down by the addition of acetone. In the reference cited above it was found that this method of preparation produced salts which were polarographically pure. Although this purity was good enough for the present study, the salts were recrystallized from absolute alcohol. This recrystallization freed the salts from most of the water and also produced a crystalline state which was more easily ground to a fine powder.

Tetramethyl and tetraethyl ammonium bromide were obtained from Eastman Chemicals. They were recrystallized from 70% alcohol followed by absolute alcohol.

Phenylhydrazine hydrochloride, 2-naphthylammonium bromide, aniline hydrobromide, semicarbazide hydrochloride, and benzidine dihydrochloride were also obtained from Eastman Chemicals. They were recrystallized once from absolute alcohol.

Hydroxylammonium bromide, ethylene diammonium bromide, benzylammonium bromide, and ethanolammonium bromide were prepared by the method given above for alkyl ammonium bromides.

Tetraallylammonium bromide was obtained from Dr. G. B. Butler of the Chemistry Department of the University of Florida. It was used as received.

Determination of Spectra

All of the spectra in this study were obtained on a Perkin-Elmer Model 21 double-beam recording spectrophotometer equipped with a calcium fluoride prism. The range of the instrument with this prism is 2-9.5 microns. The accompanying figures show the spectra which were obtained in this range on a one inch per micron scale.

All of the compounds were studied in the solid state by the potassium bromide technique. This consists of mixing a small amount of the sample with some potassium bromide, grinding the mixture to a fine powder and then pressing the mixture in a special die under high pressure to give a clear plate of potassium bromide in which the sample is dispersed.

The potassium bromide used for most of the study was Malinkrodt A.C.S. grade potassium bromide. The potassium bromide was ground for several days in a ball mill. The powdered salt, which was about 200 mesh in size, was then kept in an oven at 100°C. until needed. For the last part of the work, a small quantity of infrared grade potassium bromide from the Harshaw Chemical Company was obtained. Since this salt was already ground to about 200 mesh, it was kept in the oven as received.

It was found that satisfactory spectra were obtained when the concentration of sample in the potassium bromide was about 0.25%. Since a small particle size was necessary in order to produce satisfactory pellets, the following procedure was developed for the sample preparation. About four grams of potassium bromide, weighed to the nearest milligram, was mixed with about ten milligrams of the sample, weighed to the nearest 0.1 milligram. The mixture was placed in an agate mortar and about 2 cc. of chloroform was added. The mixture was then ground to dryness under a heat lamp. The function of the heat lamp was to prevent cooling of the sample during the evaporation of the solvent, since this might result in the condensation of water on the mixture. After grinding, the sample was left under the heat lamp for a few minutes. The sample was then placed in a small bottle and stored in a vacuum desiccator. The use of chloroform was found to give a finer and more uniform sample than was obtained by dry grinding.

The die used to prepare the pellets was one manufactured by the Perkin-Elmer Corporation, following a design suggested by Schiedt.⁽⁴⁾ It produced a pellet thirteen millimeters in diameter. The pellet could be placed in a special holder which fitted into the microcell adapter on the spectrophotometer. To prepare a pellet, about 0.35 grams of the mixture prepared as above was

weighed to the nearest milligram and placed in the die. The powder was tamped down to give an even distribution over the surface of the bottom plunger. The die was then placed in a Wabash hydraulic press of thirteen tons capacity. A slight pressure was applied. The die was evacuated for several minutes with an oil pump. A total pressure of 23,000 to 25,000 pounds was then applied to the die. After three minutes the pressure was released and the pellet removed from the die. The die was then carefully wiped off and stored in a vacuum desiccator until needed.

Although potassium bromide itself has no absorptions in the region of the infrared spectrum studied, there were two impurities which gave some trouble. The worst was water, which has two fairly strong bands at about three and six microns.⁽⁷⁾ It was not possible to remove all of the water from the potassium bromide because of its hygroscopic character. The other was potassium nitrate. Scheidt has stated that it is possible to detect potassium nitrate in potassium bromide in concentrations as low as 0.005%.⁽¹³⁾ The presence of the potassium nitrate in the sample caused some unevenness in the background of the spectra. In order to help eliminate the errors caused by these impurities, a blank pellet of potassium bromide was prepared and placed in a cell which

fitted into the window housing of the reference beam. This eliminated most of the unevenness caused by the potassium nitrate, but it did not always compensate for the water present, since the water content usually varied from sample to sample. In the accompanying figures, the water absorption at three microns is usually apparent. However, since this band did not interfere greatly with the regions of the spectra which were of the greatest interest, no further attempt to eliminate the water was made. The water band at six microns was weak and did not cause much interference. The use of a blank in the reference beam also helped to compensate for the small amount of scattering due to the potassium bromide.

Some of the pellets which were prepared were unusually cloudy. However, when the spectra were run, it was found that the greatest amount of scattering was at the high frequencies and that a translucent pellet transmitted as much light as a clear pellet below about 3000 cm^{-1} .

After the present work had been completed, Schiedt⁽¹³⁾ stated that it was possible that spectra obtained by this method were sometimes not true infrared spectra. He found that true spectra were obtained consistently only when the particle size was below 0.01 micron. In the present study, the particle size was greater than this and, since the

observation by Schiedt is not a general rule, the spectra obtained were analyzed on the assumption that they were true spectra.

CHAPTER III

DISCUSSION OF RESULTS

The 3500-3100 cm^{-1} Region

This is the region of the spectrum where the O-H and N-H stretching vibrations usually occur. Only a few of the compounds studied absorbed to any great extent here. Ethanolammonium bromide and hydroxylammonium bromide have strong bands at about 3300 cm^{-1} which can be readily assigned to the O-H stretching vibrations. (14) Phenylhydrazine hydrochloride and semicarbazide hydrochloride also have rather strong bands in this region. These bands can be assigned to the N-H stretching vibrations on the nitrogen not involved in salt formation. It has been shown by other workers (7-9) that the N-H stretching vibrations of a nitrogen involved in a salt formation do not occur in this region.

Some of the other compounds have weak bands in this region. These absorptions are probably due, for the most part, to amines formed from the decomposition of the ammonium salts.

The 3100-2800 cm^{-1} Region

In the discussion of the various absorptions in this region the following general observations will be used.

1. The asymmetric and symmetric methyl vibrations occur at about 2960 cm^{-1} and 2870 cm^{-1} respectively.
2. The asymmetric and symmetric methylene vibrations occur at about 2925 cm^{-1} and 2850 cm^{-1} respectively.
3. These frequencies are not appreciably changed as long as the carbon atom is attached to another carbon atom.
4. The influence of a non-carbon atom is usually greatly diminished on atoms beyond the adjacent ones.
5. Aromatic rings usually have a band at about 3030 cm^{-1} .

A more complete discussion of these observations has been given by Bellamy. ⁽¹⁴⁾ Other observations discussed by Bellamy will be used from time to time in the discussion below.

Since the N-H stretches in a quaternary nitrogen atom do not occur in the $3500\text{-}3100 \text{ cm}^{-1}$ region, the next most logical place to look is in this region. The ammonium ion itself absorbs at 3134 cm^{-1} and 3033 cm^{-1} . ⁽¹⁵⁾ The NH_3^+ , NH_2^+ , and NH^+ groups would be expected to absorb

at lower frequencies than this, by analogy with the corresponding CH groups. Methane, for example, absorbs at 3030 cm^{-1} and 2914 cm^{-1} , (15) which is slightly higher than the usual methyl and methylene absorptions. There is some literature data on the absorption of the NH_3^+ group. (8,9) Bellamy (14) has reviewed the data and gives a range $3130\text{--}3030\text{ cm}^{-1}$ for a band which appears in amine acids that contain the NH_3^+ group.

Table I lists the absorptions of all of the mono-substituted ammonium salts studied in the $3100\text{--}1800\text{ cm}^{-1}$ region. It can be seen that all of the compounds had at least one band above 3000 cm^{-1} , and many had two bands there. Since most of the compounds do not contain any other group which would be expected to absorb in this region, it appears that the NH_3^+ group does absorb above 3000 cm^{-1} . The presence of two bands above 3000 cm^{-1} can be explained by the fact that the NH_3^+ group would be expected to have both an asymmetric and a symmetric vibration by analogy with the methyl group, the higher frequency being due to the asymmetric vibration. The fact that two bands which could be assigned to the NH_3^+ group were not always detected may have been due to the poor resolution in this region for many of the compounds.

The NH_2^+ and NH^+ groups might be expected to absorb in this region also. However, the present study indicates

that they do not. The evidence supporting this statement is discussed in the section on the 2800-2350 cm^{-1} region. All of the compounds containing these groups were analyzed on the assumption that they do not absorb in the higher energy region.

Edsall,⁽⁶⁾ in a study on the Raman spectra of the methyl substituted ammonium salts, notes that all of the spectra had a band at about 3030 cm^{-1} which increased in intensity as the number of methyl groups was increased, the greatest intensity occurring in the tetramethyl ammonium salt. He ascribes this band to a methyl vibration since it would not occur in tetramethyl ammonium ion if it were due to an N-H vibration. The present study reveals a similar band in the infrared spectrum. In the di-, tri-, and tetramethyl ammonium salts it appears at 3026 cm^{-1} , 3017 cm^{-1} , and 3013 cm^{-1} respectively. In the methyl ammonium salt, there is a band at 3025 cm^{-1} , but it is possible that it may be due to an NH_3^+ vibration. There appear to be more bands in this region which were not resolved. The methyl vibration may be masked, since its intensity is probably weak.

Tables I and II list the bands which occurred in the spectra of the compounds studied. Each spectrum is discussed below as to the probable assignments of these

bands. In general, the spectra were rather poorly resolved, so that the list of frequencies is by no means complete.

Methyl Ammonium Bromide.--The 3086 cm^{-1} and the 3025 cm^{-1} bands were assigned to the asymmetric and symmetric NH_3^+ vibrations respectively, as was discussed above. The 2970 cm^{-1} band is probably due to the methyl group. Its position seems to indicate that it is due to the asymmetric methyl stretch. However, it has already been stated above that this absorption may occur above 3000 cm^{-1} in this compound. If this is actually the case, the 2970 cm^{-1} group may be a symmetric methyl vibration which has been shifted.

Ethyl Ammonium Bromide.--This spectrum has a band at 2949 cm^{-1} which is apparently too low for the NH_3^+ asymmetric vibration and too high for the symmetric vibration. The spectrum is too poorly resolved to detect another band in this region. However, in any case, this band is probably due to the NH_3^+ group. The bands at 2985 cm^{-1} and 2886 cm^{-1} correspond closely to the frequencies expected from the asymmetric and symmetric methyl vibrations respectively.

Propyl Ammonium Bromide.--The NH_3^+ vibrations can be assigned to the bands at 3096 cm^{-1} and 3026 cm^{-1} in this compound. The 2996 cm^{-1} and 2895 cm^{-1} bands are

probably due to the methyl group vibrations. The 2833 cm^{-1} band is at a position consistent with a symmetric methylene vibration.

Isopropyl Ammonium Bromide.--The 3077 cm^{-1} and 3025 cm^{-1} bands can be assigned to the NH_3^+ group. The origin of the 2941 cm^{-1} band is unknown. The fact that it is an intense band indicates that it probably arises from the methyl groups.

Butyl Ammonium Bromide.--The NH_3^+ bands appear at 3091 cm^{-1} and 3021 cm^{-1} in this spectrum. The 2964 cm^{-1} band is probably due to an asymmetric methyl vibration. The origin of the 2824 cm^{-1} band is not clear, although it may be due to a symmetric methylene vibration on the carbon adjacent to the nitrogen. The symmetric vibration of the other methylene groups and of the methyl group would be expected at a higher frequency.

2-Bromoethyl Ammonium Bromide.--The NH_3^+ vibrations appear at 3081 cm^{-1} and 3003 cm^{-1} in this spectrum. The 2933 cm^{-1} band can be assigned to an asymmetric methylene vibration since no other vibration is to be expected in this region from this compound.

Ethanolammonium Bromide.--The 3077 cm^{-1} and the 3046 cm^{-1} band can be assigned to the NH_3^+ group. The 2907 cm^{-1} and the 2943 cm^{-1} bands are probably due to the

asymmetric methylene vibrations although it is not possible to decide which band is due to which methylene group.

Ethylene Diammonium Bromide.--There is no resolved band in this spectrum which may be assigned to the NH_3^+ asymmetric vibration. However, the spectrum indicates that there is an absorption in the expected region. The 3016 cm^{-1} band can be assigned to the symmetric NH_3^+ vibration. The 2924 cm^{-1} and 2903 cm^{-1} bands are probably due to the asymmetric methylene vibrations, the appearance of two bands arising from an interaction between the two groups.

Hydroxylammonium Chloride.--This spectrum was not resolved sufficiently in this region for any distinct bands to be observed.

Semicarbazide Hydrochloride.--The spectrum has a band at 3049 cm^{-1} which could be assigned to one of the NH_3^+ vibrations. There does not appear to be any proof for the assignment of the other bands in the spectrum.

Phenylhydrazine Hydrochloride.--Either the 3026 cm^{-1} or the 3009 cm^{-1} band is probably due to the ring vibration. The spectrum shows that the 3009 cm^{-1} band is much sharper than the 3026 cm^{-1} band which indicates that the 3009 cm^{-1} band is probably due to this ring vibration. The 3026 cm^{-1} band could then be assigned to the NH_3^+ group. There is a slight shoulder on the

main absorption which may be due to the other NH_3^+ vibration which is expected in this region. There appears to be no convenient assignment for the other bands.

Aniline Hydrobromide.--This spectrum was too poorly resolved for any distinct bands to be observed.

Benzyl Ammonium Bromide.--This spectrum was also too poorly resolved to be of any use in this region.

Benzidene Dihydrochloride.--Only two definite bands could be distinguished in this region. The 3049 cm^{-1} band could be due to either the NH_3^+ group or to a ring vibration. No assignment could be made for the 2852 cm^{-1} band.

2-Naphthyl Ammonium Bromide.--The band at 3058 cm^{-1} is probably due to a ring vibration. The symmetric NH_3^+ vibration may appear at 3017 cm^{-1} , although this may also be due to a ring vibration. The origin of the other bands in the spectrum is not known.

Dimethyl Ammonium Bromide.--The 3026 cm^{-1} band has already been assigned to the methyl group. The 2976 cm^{-1} band is probably due to the methyl groups. No assignment could be made for the other bands in this spectrum.

Diethyl Ammonium Bromide.--The 2967 cm^{-1} and 2861 cm^{-1} bands probably arise from the asymmetric and symmetric methyl vibrations respectively. The 2909 cm^{-1} and the 2827 cm^{-1} bands correspond closely to the

asymmetric and symmetric methylene vibrations. They have apparently been shifted to a slightly lower frequency by the adjacent nitrogen atom.

Dipropyl Ammonium Bromide.--The methyl group vibrations can be identified with the bands at 2971 cm^{-1} and 2884 cm^{-1} . The 2817 cm^{-1} band may be due to a symmetric methylene vibration which has been shifted to a lower frequency by the adjacent NH_3^+ group.

Diisopropyl Ammonium Bromide.--The 2972 cm^{-1} band corresponds closely to an asymmetric methyl vibration. The 2911 and 2842 cm^{-1} bands may be due to the symmetric vibration which has been split into two components. The midpoint between these two bands is close to the expected frequency for this vibration.

Diallyl Ammonium Bromide.--The 3081 cm^{-1} band is at the frequency expected for a terminal vinyl stretch. (14) The 2941 cm^{-1} and 2892 cm^{-1} bands may be due to a Fermi resonance of the expected asymmetric methylene vibration at about 2925 cm^{-1} and the first overtone of the 1464 cm^{-1} band. An alternative explanation would be to assign one of the bands to the asymmetric methylene vibration and not assign the other. Neither band, however, appears at a frequency to be expected from this vibration.

Trimethyl Ammonium Bromide.--The 3017 cm^{-1} band has already been assigned to the methyl group. The 2959 cm^{-1} band is also probably due to the methyl groups, although whether it is a normal asymmetric vibration or a shifted symmetric vibration cannot be determined. The origin of the 2933 cm^{-1} band could not be determined.

Triethyl Ammonium Bromide.--The expected methyl group vibrations may be identified at 2976 cm^{-1} and 2885 cm^{-1} . The 2941 cm^{-1} and the 2807 cm^{-1} bands may arise from the methylene groups, although the first appears to be too high and the second too low for the expected vibrations.

Tripropyl Ammonium Bromide.--The 2970 cm^{-1} and the 2890 cm^{-1} bands can be identified with the asymmetric and symmetric methyl vibrations respectively. The 2941 cm^{-1} band corresponds to an asymmetric methylene vibration.

Tetramethyl Ammonium Bromide.--The 3013 cm^{-1} band has already been assigned to the methyl group. The 2957 cm^{-1} band is also probably due to the methyl group. The origin of the other bands could not be determined.

Tetraethyl Ammonium Bromide.--The only band of any great intensity in this region is the 2990 cm^{-1} band. This may be due to an asymmetric methyl vibration. The origin of the other bands is not certain. The 2924 cm^{-1} and the 2913 cm^{-1} bands may be due to methylene vibrations

since they appear at frequencies close to those expected from this group. The 2956 cm^{-1} band may arise from another methyl vibration.

Tetraallyl Ammonium Bromide.---The 3095 cm^{-1} band is due to the terminal vinyl stretch. (14) The 3021 cm^{-1} band is probably due to the $=\text{CH}$ -stretch. The origin of the other bands could not be determined.

While many of the assignments made above are very tentative, a few general observations can be made. The NH_3^+ group apparently has two bands in the $3100\text{-}3000\text{ cm}^{-1}$ region in the alkyl substituted ammonium compounds. Whether this was also true in the other monosubstituted compounds studied could not be determined conclusively. In particular, the compounds containing aromatic rings also absorb in this region, which increases the difficulty of assignment. In addition, many of the non-alkyl substituted compounds had many unresolved absorptions throughout this region. Further work will have to be done on this type of compound in order to determine whether the NH_3^+ group absorbs in the same range as in the alkyl-substituted compounds. The spectra of the compounds which contain a mobile electron pair adjacent to the nitrogen seem to have a distinctly different spectrum in the $2800\text{-}2350\text{ cm}^{-1}$ region, which is discussed in the next section. This indicates that the

NH_3^+ group in this type of compound is different from the same group in other types of compounds.

The NH_3^+ group appears to raise the frequency of a methyl group directly attached to the nitrogen. The effect of the NH_3^+ group on an adjacent methylene group does not appear to be clear-cut, however. In some compounds the frequencies appear to be raised and in others they appear to be lowered.

TABLE I

THE SPECTRAL BANDS OF SOME MONOSUBSTITUTED AMMONIUM
SALTS IN THE 3100-2800 cm^{-1} REGION

Compound		Frequency in cm^{-1} (a)				
$\text{CH}_3\text{NH}_3\text{Br}$	3086s 3025m 2970w					
$\text{C}_2\text{H}_5\text{NH}_3\text{Br}$	3049s	2985s		2886w		
$\text{C}_3\text{H}_7\text{NH}_3\text{Br}$	3096s 3026s	2956s		2895s	2833m	
$(\text{CH}_3)_2\text{CHNH}_3\text{Br}$	3077s 3025s		2941s			
$\text{C}_4\text{H}_9\text{NH}_3\text{Br}$	3091s 2021s	2964s		2824m		
$\text{BrCH}_2\text{CH}_2\text{NH}_3\text{Br}$	3081m 3003s		2933m			
$\text{HOCH}_2\text{CH}_2\text{NH}_3\text{Br}$	3077m 3046s		2907m		2843w	
HONH_3Br	See text					
$(\text{CH}_2\text{NH}_3\text{Br})_2$		3016s 2924s	2903m			
$\text{H}_2\text{NCONHNH}_3\text{Cl}$	3049m		2972m 2915m	2871m		
$\text{C}_6\text{H}_5\text{NHNH}_3\text{Cl}$	3026s 3009s	2955s		2853s		
$\text{C}_6\text{H}_5\text{NH}_3\text{Br}$	See text					
$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3\text{Br}$	See text					
$(\text{C}_6\text{H}_4\text{NH}_3\text{Cl})_2$	3049s			2852s		
$\text{C}_{10}\text{H}_7\text{NH}_3\text{Br}$	3058w 3017m		2906s 2865s	2813s		

(a) The letters w, m, and s which follow the frequency of the bands indicate the intensity of the band and stand for weak, medium, and strong intensity respectively.

TABLE II

THE SPECTRAL BANDS OF SOME DI-, TRI-, AND TETRA-SUBSTITUTED AMMONIUM SALTS IN THE 3100-2800 cm^{-1} REGION

Compound	Frequency in cm^{-1} (a)			
$(\text{CH}_3)_2\text{NH}_2\text{Br}$	3026m	2976s	2924w	2895w
$(\text{C}_2\text{H}_5)_2\text{NH}_2\text{Br}$		2967s	2909s	2861s 2827s
$(\text{C}_3\text{H}_7)_2\text{NH}_2\text{Br}$		2971s		2884m 2817s
$[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2\text{Br}$		2972s	2911s	2842s
$(\text{CH}_2=\text{CHCH}_2)_2\text{NH}_2\text{Br}$	3081m		2941s	2892m
$(\text{CH}_3)_3\text{NHBBr}$	3017m	2959s	2933w	
$(\text{C}_2\text{H}_5)_3\text{NHBBr}$		2976m	2941s	2885w 2807w
$(\text{C}_3\text{H}_7)_3\text{NHBBr}$		2970s	2941m	2890m
$(\text{CH}_3)_4\text{NBr}$	3013m	2957w	2915w	2839w
$(\text{C}_2\text{H}_5)_4\text{NBr}$		2990m	2956w	2924w 2913w
$(\text{CH}_2=\text{CHCH}_2)_4\text{NBr}$	3095m 3021m	2963s		2899w

(a) The letters w, m, and s which follow the frequency of the bands indicate the intensity of the band and stand for weak, medium, and strong intensity respectively.

The 2800-2350 cm^{-1} Region

Very few fundamentals occur in this region of the infrared spectrum. It is known that sulfur-hydrogen and phosphogorous-hydrogen stretches occur here, (14) but no structure of this type occurs in the compounds studied. It has been noted that amino acids and their hydrochlorides absorb extensively in this region, but no characterization of these absorptions has been made. It is supposed that these bands arise from the NH groupings since they do not appear to be present in the salts of the amino acids. In the present study, all of the compounds except for the tetrasubstituted compounds have bands in this region. This supports the assumption that these bands arise from the NH groups. Table III lists the strong and medium absorptions in this region. The table is limited to these bands because of the multiplicity of weak bands which occur. Most of the bands are probably due to interaction effects of the NH groups. However, there appear to be possible assignments for some of the stronger bands. These possible assignments are discussed below.

None of the monoalkyl substituted ammonium salts had any strong bands in this region. For this reason they do not appear in the table. All of the monosubstituted compounds which do appear in this table have one structural

feature in common; there is at least one pair of relatively mobile electrons on the atom adjacent to the NH_3^+ group. In hydroxylammonium bromide the oxygen atom has two pairs of unbonded electrons. In phenylhydrazine hydrochloride and semicarbazide hydrochloride, the nitrogen atom adjacent to the NH_3^+ group has one pair of unbonded electrons. In aniline hydrobromide, benzidine dihydrochloride, and 2-naphthyl ammonium bromide there is a double bond on the adjacent carbon which can furnish a pair of relatively mobile electrons. This suggests that the strong vibrations in these compounds are due to an NH_3^+ vibration which has been shifted by the presence of the mobile electrons. The positively charged nitrogen would attract these mobile electrons, which would increase the electron density around the nitrogen. The effective charge of the nitrogen would be decreased, and this would lead to a weakening of the NH bonds. It is interesting to note that the above compounds are stronger acids than the other monosubstituted compounds. For the compounds discussed above, $-\log K_a$ varies from 9.44 to 10.75. ⁽¹⁶⁾ In the other monosubstituted compounds, except for benzylammonium bromide, it varies from 3.43 to 6.03. ⁽¹⁶⁾ Benzylammonium bromide appears to be an anomalous case. While it has an acid constant of 9.3, it also has several medium intensity bands in this region, even with no mobile electrons

on the adjacent carbon atom. It is possible that the effect of the aromatic ring is transmitted through the methylene group so that a shift in electron density would also take place in this compound.

All of the di- and tri-substituted compounds have at least one, and usually more than one, strong band in this region. The intensities of these bands indicate that they are probably fundamentals. The absence of any bands which could be assigned to the NH_2^+ and NH^+ groups in the $3100\text{-}2800\text{ cm}^{-1}$ region indicates that they probably arise from these structures. However, an explanation of the unexpectedly low frequency was sought. In general, alkyl groups are electron releasing groups. The effect of this electron releasing ability is to increase the electron density around the adjacent atoms which would result in a lowering of the hydrogen stretches on these atoms. This effect is demonstrated by the fact that, in hydrocarbons, the methyl group absorbs at a higher frequency than the methylene group, which in turn absorbs at a higher frequency than the tertiary CH group. Table III shows that this holds generally for the NH groups also. The NH_2^+ group has already been shown to absorb above 3000 cm^{-1} . The disubstituted compounds appear to absorb in the region $2801\text{-}2764\text{ cm}^{-1}$ while the trisubstituted compounds appear to absorb in the $2747\text{-}2632\text{ cm}^{-1}$ region. The unusually

large shift in going from the NH_2^+ group to the NH_2^+ group is probably due to the fact that the positive charge on the nitrogen would tend to attract the electrons which the alkyl group releases. This would tend to exaggerate the electron releasing power of the alkyl group. The fact that another large shift does not occur in going from the NH_2^+ group to the NH^+ group may be due to the electron density having neared the saturation point in the NH_2^+ group.

The NH_2^+ group would be expected to have another band in this region. It may be identified with one of the bands which occur in the $2550\text{-}2350\text{ cm}^{-1}$ region. The NH^+ group would be expected to have only one band in this region. The assignment of the other bands was not possible. All three of the trisubstituted compounds had a strong band in the $2530\text{-}2479\text{ cm}^{-1}$ region. A larger number of compounds of these types would have to be studied before any general conclusions could be made about the expected ranges of the bands which occur.

TABLE III

THE MEDIUM AND STRONG SPECTRAL BANDS OF SOME SUBSTITUTED
AMMONIUM SALTS IN THE 2800-2350 cm^{-1} REGION

Compound	Frequency in cm^{-1} (a)			
HONH_3Br	2758m	2710m	2667s	
$\text{H}_2\text{NCONHNH}_3\text{Cl}$	2762m		2672s	
$\text{C}_6\text{H}_5\text{NHNH}_3\text{Cl}$			2699s	
$\text{C}_{10}\text{H}_7\text{NH}_3\text{Br}$		2706s	2661m	2601m 2581s
$(\text{C}_6\text{H}_4\text{NH}_3\text{Cl})_2$				2554s
$\text{C}_6\text{H}_5\text{NH}_3\text{Br}$				2581s
$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3\text{Br}$		2681m		2551m
$(\text{CH}_3)_2\text{NH}_2\text{Br}$	2782s			2447s
$(\text{C}_2\text{H}_5)_2\text{NH}_2\text{Br}$	2780s	2751s		2476m 2371m
$(\text{C}_3\text{H}_7)_2\text{NH}_2\text{Br}$	2801s			2529m 2417m
$[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2\text{Br}$	2764s	2728s		2486s 2431m
$(\text{CH}=\text{CHCH}_2)_2\text{NH}_2\text{Br}$	2797s	2728m		2561m 2412m
$(\text{CH}_3)_3\text{NHBr}$		2703s		2479m
$(\text{C}_2\text{H}_5)_3\text{NHBr}$		2747s 2682s		2499s
$(\text{C}_3\text{H}_7)_3\text{NHBr}$	2762m	2717m 2632s	2611m	2503s

(a) The letters m and s following the frequency of the bands indicate the intensity of the band and stand for medium and strong intensity respectively.

The 1700-1600 cm^{-1} Region

Various types of double bond stretches occur in this region of the spectrum. A few other types of vibrations occur here also. Since only a few of the compounds studied had any significant absorptions in this region, they can be discussed individually.

Diallyl ammonium bromide absorbs at 1652 cm^{-1} , while tetraallyl ammonium bromide absorbs at 1645 cm^{-1} . This band is due to the carbon-carbon double bond stretching which occurs in propene at 1647 cm^{-1} . (15)

Semicarbazide hydrochloride has two strong bands at 1691 cm^{-1} and 1686 cm^{-1} . These bands are probably due to the carbonyl group which, in urea, absorbs at 1689 cm^{-1} . (7) The doublet may arise from either an interaction between the carbonyl group and some other part of the molecule or from the presence of an enol form that would give rise to a $\text{C}=\text{N}$ structure, which would be expected to absorb in this region. A third possibility is that one of the bands is due to an NH deformation on one of the nitrogens not involved in the salt formation, since the NH deformation in amides sometimes absorbs in this region. (7,14)

All of the other compounds which absorb in this region are aromatic and would ordinarily be expected to have one or two bands close to 1600 cm^{-1} , depending upon whether the ring is conjugated or not. Benzidine dihydro-

chloride and phenylhydrazine hydrochloride have sharp bands at 1600 cm^{-1} and 1613 cm^{-1} respectively. Aniline hydrobromide has three bands at 1631 cm^{-1} , 1616 cm^{-1} , and 1603 cm^{-1} . The spectrum of 2-naphthyl ammonium bromide has two bands at 1643 cm^{-1} and 1617 cm^{-1} . All of these bands can be assigned to the aromatic double bond vibrations except perhaps for one of the aniline hydrobromide bands. Since only two bands at the most would be expected in this region from the aromatic ring, the third band may be due to an NH_3^+ deformation which has been shifted to a higher frequency than usual. This possibility is discussed more fully in the next section.

Benzyl ammonium bromide would be expected to absorb in this region. However, there appears to be no band in the spectrum here. There is a sharp band at 1591 cm^{-1} which may be due to an aromatic ring vibration. This band is discussed more fully in the next section.

The 1600-1490 cm^{-1} Region

It has been shown by other workers that amino acids and their hydrochlorides which can possess the NH_3^+ group usually have two bands in this region. (7,9) There appears to be some doubt as to the exact position of these bands. Bellamy⁽¹⁴⁾ quotes a range of 1660-1610 cm^{-1} for the first band and 1550-1485 cm^{-1} for the second. These ranges apparently refer only to amino acids because Randall⁽⁷⁾ quotes the ranges 1630-1570 cm^{-1} and 1546-1499 cm^{-1} for such compounds, while he quotes the ranges 1610-1590 cm^{-1} and 1522-1483 cm^{-1} for the hydrochlorides.

The assignment of both of these bands to the NH_3^+ group has not been definitely established. Randall⁽⁷⁾ for example, assigns only the first band to this group and does not assign the second. The possibility that both are due to the NH_3^+ group is indicated by the fact that both are absent in the spectra of the sodium salts of the amino acids. It is to be expected that the NH_3^+ group would have both asymmetric and symmetric deformations corresponding to the same deformations in the methyl group.

Table IV lists the absorptions in this region of the monosubstituted ammonium salts. Only the well-defined bands are listed. Many of the bands had shoulders of varying intensity which were omitted.

For the first nine compounds in the table the assignment of the bands was relatively simple. In these compounds no fundamentals would be expected other than those due to the NH_3^+ group. Hence, all of the bands in this region for these compounds were assigned to this group. One anomalous case is apparent. Ethyl ammonium bromide has only one band in this region, at 1599 cm^{-1} , whereas all of the other compounds had at least two. The absence of a band near 1500 cm^{-1} is particularly puzzling because this band is usually the strongest band in the region in the other compounds. The missing band may be identified with either the shoulder at 1493 cm^{-1} or the shoulder at 1481 cm^{-1} . The first band is in the expected range but appears to be too weak. The second is stronger but appears at a rather low frequency.

Some of these nine compounds show more than two bands in this region. These may arise from an interaction of the groups in the solid state. In most cases, however, the highest and lowest frequencies were the strongest and, therefore, were assigned to the asymmetric and NH_3^+ deformations respectively.

For the remaining six compounds the assignment is complicated by the fact that other absorptions are expected in this region. For semicarbazide, an absorption around 1550 cm^{-1} is to be expected from the secondary amide group. The spectrum has two bands at 1546 cm^{-1} and 1521 cm^{-1} , either

or both of which is probably due to this group. The bands at 1584 cm^{-1} and 1493 cm^{-1} were assigned to the NH_3^+ deformations.

The remaining five compounds in Table IV all contain an aromatic ring. According to Bellamy⁽¹⁴⁾ an aromatic ring usually has two bands in this region, one near 1600 cm^{-1} and the other near 1500 cm^{-1} . In addition, a band near 1580 cm^{-1} often occurs, particularly if the ring is conjugated in some way. For reasons which are apparent in the following discussion, these five compounds were split into two groups. The first group consisted of phenylhydrazine hydrochloride and benzyl ammonium bromide in which the NH_3^+ group is insulated from the aromatic ring by an intervening group. The second group consists of aniline hydrobromide, 2-naphthyl ammonium bromide, and benzidine dihydrochloride in which the NH_3^+ group is attached directly to the ring.

In the first group it might be expected that the NH_3^+ deformations would occur at the usual frequencies because of the insulating effect of the intervening group, and this appears to be the case. In phenylhydrazine hydrochloride, the highest frequency ring vibration has already been identified at 1613 cm^{-1} . The band at 1584 cm^{-1} appears to have a rather strong shoulder on the high frequency side. If the 1584 cm^{-1} band is assigned to the NH_3^+ asymmetric

deformation, then this shoulder can be explained by the fact that the unbonded electron pair in the nitrogen next to the ring is in a conjugated position and may be expected to give rise to a band in this region. It is possible that the assignments should be reversed, assigning the shoulder to the NH_3^+ group and the main band to the ring vibration. In any case, it appears that the NH_3^+ deformation occurs in the expected range. At the lower end of this region, phenylhydrazine hydrochloride has two strong bands at 1503 cm^{-1} and 1495 cm^{-1} . These bands may be assigned to the aromatic ring vibration and the NH_3^+ symmetric deformation, both of which would be expected in this range. No decision could be made as to which band is due to which vibration. In this case also, the NH_3 deformation appears in the expected range. The origin of the 1546 cm^{-1} and the 1521 cm^{-1} bands in this spectrum could not be determined.

In benzylammonium bromide, a band appears at 1591 cm^{-1} which one might want to assign to the NH_3^+ deformation. However, as was noted in the previous section, no band appears above 1600 cm^{-1} which could be assigned to the expected ring vibration. The sharpness of the 1591 cm^{-1} band indicates that it is probably due to the ring vibration. There is a weak shoulder at

1580 cm^{-1} which is probably the NH_3^+ asymmetric deformation. In the lower part of this region, only one well defined band appears, at 1498 cm^{-1} where two are expected. Bellamy⁽¹⁴⁾ states that the 1500 cm^{-1} band in aromatic rings is usually stronger than the 1600 cm^{-1} band and that its frequency shifts usually parallel the 1600 cm^{-1} band. Since the 1600 cm^{-1} band has apparently been shifted to a lower frequency, the 1500 cm^{-1} band may also be found at a lower frequency. In fact, a strong band does appear at 1475 cm^{-1} which is apparently the ring vibration. Support for this assignment is found in the fact that three strong bands appear at about 1475-1450 cm^{-1} where only one or at the most two are to be expected. The reason for this is discussed in the next section. In addition, the 1475 cm^{-1} band appears to be slightly stronger than the 1591 cm^{-1} band, which is to be expected if this assignment is correct. Since the ring vibrations have now been identified, the 1498 cm^{-1} band can be assigned to the symmetric NH_3^+ deformation. The origin of the weak band at 1536 cm^{-1} is not known, although its broad shape indicates that it may be an overtone or a combination band.

In the compounds where the NH_3^+ group is attached directly to the aromatic ring, it was difficult to identify the NH_3^+ deformations. In aniline hydrobromide, the ring vibration can probably be identified with the bands at

1603 cm^{-1} and 1495 cm^{-1} . Then the NH_3^+ deformations could be identified with the bands at 1563 cm^{-1} and 1515 cm^{-1} . There are several other possibilities, however. The assignment of the two lower frequency bands could be reversed. The asymmetric NH_3^+ deformation could also be identified with a shoulder at 1592 cm^{-1} .

In benzidine dihydrochloride and 2-naphthyl ammonium bromide, the ring is conjugated so that three bands due to the aromatic rings are to be expected in this region. Definite assignments of the NH_3^+ deformations could not be made without further study on this same type of compound. If one assumes that the broader bands in this region are due to the NH_3^+ deformations, it appears that these vibrations come at a slightly lower frequency than usual.

There is some evidence that the NH_2^+ group should also absorb in this region. Randall⁽⁷⁾ has assigned a band in the range 1637-1553 cm^{-1} in some N-substituted amino acids to the NH_2^+ group. Table VI lists the absorptions of the polysubstituted ammonium compounds studied in this region. It can be seen that only the disubstituted compounds in this table absorb above 1500 cm^{-1} . This band, which occurs in the range 1589-1570 cm^{-1} , can therefore be assigned to the NH_2^+ group.

TABLE IV

THE SPECTRAL BANDS OF SOME MONOSUBSTITUTED AMMONIUM
COMPOUNDS IN THE 1600-1500 cm^{-1} REGION

Compound	Frequency in cm^{-1} (a)		
$\text{CH}_3\text{NH}_3\text{Br}$	1579m		1499s
$\text{C}_2\text{H}_5\text{NH}_3\text{Br}$	1599m		
$\text{C}_3\text{H}_7\text{NH}_3\text{Br}$	1569s		1504s
$(\text{CH}_3)_2\text{CHNH}_3\text{Br}$	1581s		1503s
$\text{C}_4\text{H}_9\text{NH}_3\text{Br}$	1589m		1503s
$\text{BrCH}_2\text{CH}_2\text{NH}_3\text{Br}$	1581s		1492s
$(\text{CH}_2\text{NH}_3\text{Br})_2$	1599m	1564m 1511m	1505s
HONH_3Br		1569m 1548w	1493m
$\text{H}_2\text{NC}(=\text{O})\text{NHNH}_3\text{Cl}$	1584s	1564m 1520	1493m
$\text{C}_6\text{H}_5\text{NHNH}_3\text{Cl}$	1584s	1546m 1521m	1503s 1495s
$\text{C}_6\text{H}_5\text{NH}_3\text{Br}$		1563s 1515m	1495s
$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3\text{Br}$	1591s		1536w 1498m
$(\text{C}_6\text{H}_4\text{NH}_3\text{Cl})_2$		1555m 1517m	1496s
$\text{C}_{10}\text{H}_7\text{NH}_3\text{Br}$	1594m 1574m		1504s

(a) The letters w, m, and s which follow the frequencies of the bands indicate the intensity of the bands and stand for weak, medium and strong intensities respectively.

The 1490-1350 cm^{-1} Region

The methyl and methylene deformations usually occur in this region. Certain types of skeletal vibrations also sometimes occur here. Because of the wide ranges and large shifts which are characteristic of skeletal vibrations, the only definite assignments which can be made are for the deformation vibrations. The following observations were used in the assignment of bands.

1. The methyl deformations usually occur in the ranges 1470-1430 cm^{-1} and 1380-1370 cm^{-1} .
2. The methylene deformation usually occurs in the range 1445-1485 cm^{-1} .

These observations have been discussed fully by Bellamy. (14) Richards and Thompson (17) have observed that these bands are often split in the solid state. This observation has been confirmed by other workers. (18,19) MacMurray and Thornton, (20) among others, also state that the 1380 cm^{-1} band is often split when two methyl groups are attached to the same carbon atom.

Tables V and VI list the bands in this region which occur in the spectra of the compounds studied. Only well-defined bands are listed.

Methyl Ammonium Bromide.--Two methyl deformations are to be expected in this region. The 1409 cm^{-1} band is probably due to the symmetric deformation while the asymmetric

deformation is apparently obscured by the strong band at 1499 cm^{-1} .

Ethyl Ammonium Bromide.--Methyl and methylene deformations are to be expected. Since the methylene group usually absorbs at a higher frequency than the methyl group, the 1473 cm^{-1} band was assigned to the methylene deformation and the 1466 cm^{-1} band to the methyl asymmetric deformation. Both of the remaining bands may be due to the symmetric methyl vibration. The split is due to the fact that the vibration may be either in or out of phase with the corresponding vibration of the NH_3^+ group which is attached to the same carbon atom.

Propyl Ammonium Bromide.--Both methyl and methylene deformations are to be expected. The methyl deformations may be identified with the bands at 1463 cm^{-1} and 1399 cm^{-1} . The 1466 cm^{-1} band is probably due to the methylene group adjacent to the methyl group since it appears from the spectra already discussed above that the methylene adjacent to the nitrogen absorbs at a slightly higher frequency. There is a shoulder on the low frequency side of the 1504 cm^{-1} band which may be identified with this methylene group.

Isopropyl Ammonium Bromide.--Only methyl vibrations are to be expected since the tertiary CH usually is weak and occurs below 1350 cm^{-1} . The 1474 cm^{-1} band is probably

due to the asymmetric methyl deformation. The bands at 1400 cm^{-1} and 1381 cm^{-1} are probably due to a splitting of the symmetric methyl deformation because of the occurrence of two methyl groups on the same carbon atom.

Butyl Ammonium Bromide.--Methyl and Methylene deformations are to be expected. The spectrum was not well resolved in the upper part of this region. The 1467 cm^{-1} band may be due to one of the methylene groups. The 1400 cm^{-1} and 1381 cm^{-1} bands are apparently due to a split of the symmetric methyl deformation.

2-Bromoethyl Ammonium Bromide.--Only methylene deformations should occur. The 1485 cm^{-1} band was assigned to the methylene adjacent to the nitrogen in keeping with the observation made above that the nitrogen appears to increase the frequency of adjacent groups. The 1427 cm^{-1} band would then be assigned to the methylene group adjacent to the bromine atom. This latter assignment is supported by the observation of Brown and Sheppard, ⁽²¹⁾ that 1,2-dibromoethane absorbs at 1435 cm^{-1} , below the usual frequency for a methylene vibration.

Ethanol Ammonium Bromide.--Only methylene vibrations are to be expected. The 1478 cm^{-1} band is probably due to the methylene adjacent to the nitrogen while the 1458 cm^{-1} band is probably due to the methylene group adjacent to the hydroxyl group.

Ethylene Diammonium Bromide.--Methylene deformations only are to be expected. Only one band is readily apparent in this spectrum, at 1351 cm^{-1} , which appears to be too low for the methylene deformation. Apparently the methylene deformation is masked by the strong band at 1505 cm^{-1} , which has a very broad shoulder on the low frequency side.

Hydroxylammonium Bromide.--No deformation vibrations are to be expected in this region. The two strong bands at 1477 cm^{-1} and 1460 cm^{-1} are most probably due to the N-O stretching vibration.

Semicarbazide Hydrochloride.--The only bands which might be expected in this region are the C-N stretches. (14) The bands at 1447 cm^{-1} and 1385 cm^{-1} may arise from these vibrations.

Phenylhydrazine Hydrochloride.--There are no apparent vibrations to be expected in this region. The band at 1449 cm^{-1} may be due to a C-N or an N-N stretching vibration. The position of these vibrations in other compounds has not been very well defined.

Benzyl Ammonium Bromide.--A methylene deformation is to be expected in this region. In the previous section, the 1475 cm^{-1} band was assigned to a ring vibration. The 1466 cm^{-1} and 1456 cm^{-1} bands are probably due to a split methylene vibration. The origin of the 1385 cm^{-1} band is not known.

2-Naphthyl Ammonium Bromide.--No deformations are to be expected in this region. The origin of the bands which do occur is not known.

Dimethyl Ammonium Bromide.--Only methyl deformations are to be expected. They may be identified with the bands at 1471 cm^{-1} and 1408 cm^{-1} . The origin of the other bands is not known.

Diethyl Ammonium Bromide.--Methyl and methylene deformations are to be expected. The band at 1483 cm^{-1} is probably due to the methylene deformation. The other four bands may all be due to the methyl groups. The pair at 1462 cm^{-1} and 1440 cm^{-1} can be assigned to a split asymmetric deformation, while the 1393 cm^{-1} and 1378 cm^{-1} bands can be assigned to a split symmetric deformation.

Dipropyl Ammonium Bromide.--Both methyl and methylene deformations are to be expected. The 1475 cm^{-1} band is probably due to the methylene adjacent to the nitrogen atom, while the 1461 cm^{-1} band is due to the other methylene group. The 1453 cm^{-1} band is at the correct frequency for an asymmetric methyl deformation. The origin of the 1416 cm^{-1} band is uncertain, since it appears to be too high for the symmetric methyl deformation.

Diisopropyl Ammonium Bromide.--Only methyl deformations are to be expected. The 1470 cm^{-1} and 1444 cm^{-1} bands may be due to a split asymmetric methyl deformation.

The symmetric vibration appears to be split, as expected, with bands appearing at 1403 cm^{-1} and 1386 cm^{-1} . The origin of the 1421 cm^{-1} band is not known.

Diallyl Ammonium Bromide.--Two types of methylene deformations are to be expected. The 1464 cm^{-1} band is probably due to the methylene adjacent to the nitrogen atom. According to Bellamy, ⁽¹⁴⁾ the $=\text{CH}_2$ group absorbs strongly in the range $1420\text{--}1410\text{ cm}^{-1}$. The only other strong band in this region is at 1437 cm^{-1} which is most probably the $=\text{CH}_2$ deformation although the frequency appears to be a little high. The origin of the 1380 cm^{-1} band is not known.

Trimethyl Ammonium Bromide.--Only methyl deformations are to be expected. The 1478 cm^{-1} band is probably the asymmetric methyl deformation. The bands at 1430 cm^{-1} and 1403 cm^{-1} may be associated with a split symmetric methyl deformation. Another assignment is possible for the 1430 cm^{-1} band. All three of the trisubstituted compounds studied have a band in the range $1430\text{--}1444\text{ cm}^{-1}$, a range in which no bands appear consistently in the other spectra. Since the only common group in these compounds which does not appear in the other compounds is the NH^+ group, it is possible that this band may be due to this group. The fact that this frequency is much lower than that assigned to the NH_3^+ and NH_2^+ groups is to be expected.

In the corresponding CH group, the deformation occurs at about 1340 cm^{-1} , which is much lower than the methyl and methylene deformations. The relatively great intensity, as compared to the CH group, may be due to the fact that the nitrogen atom is charged. If the NH^+ and CH groups underwent the same vibration, the change in dipole moment for the NH^+ group would be greater than for the CH group. Since the intensity depends to a large extent upon the change in dipole moment, ⁽¹⁵⁾ this would result in a greater intensity for the NH^+ vibration.

Triethyl Ammonium Bromide.--Both methylene and methyl deformations are to be expected. The band at 1477 cm^{-1} is probably due to the methylene deformation. The 1436 cm^{-1} band can be assigned to the NH^+ group for the reasons given in the preceding paragraph. The symmetric methyl deformation may be due to any or all of the three bands at 1403 cm^{-1} , 1388 cm^{-1} and 1378 cm^{-1} . The 1403 cm^{-1} band could be a perturbed methyl deformation while the other two bands can then be assigned to a split symmetric methyl deformation. No band is listed in the table which could correspond to the expected asymmetric methyl deformation. However, a shoulder appears on the low frequency side of the 1477 cm^{-1} band which is probably due to this vibration.

Tripropyl Ammonium Bromide.--Both methylene and methyl deformations are to be expected. The 1474 cm^{-1} band is probably due to the methylene adjacent to the nitrogen atom. The 1464 cm^{-1} band can be due to either the other methylene group or the asymmetric methyl deformation. This band does not appear to be well resolved so that it is possible that both bands occur here. The 1403 cm^{-1} and 1381 cm^{-1} bands may be due to a split symmetric methyl deformation. The 1444 cm^{-1} band can be assigned to the NH^+ group, as was explained above.

Tetramethyl Ammonium Bromide.--Only methyl deformations are to be expected. The 1488 cm^{-1} band can be assigned to the asymmetric methyl deformation. The pair of bands at 1405 cm^{-1} and 1399 cm^{-1} is probably due to a split symmetric methyl deformation.

Tetraethyl Ammonium Bromide.--Both methylene and methyl deformations are to be expected. The 1498 cm^{-1} band is probably due to the methylene deformation, although the frequency appears to be a little higher than usual. The 1449 cm^{-1} band can be assigned to the asymmetric methyl deformation. The other three bands may all be due to the symmetric methyl deformation. The 1376 cm^{-1} band is probably the unperturbed vibration.

Tetraallyl Ammonium Bromide.--Two types of methylene deformations are to be expected. The 1464 cm^{-1} band can be assigned to the methylene adjacent to the nitrogen atom. The 1426 cm^{-1} band is in the correct position for the $=\text{CH}_2$ deformation. The origin of the 1371 cm^{-1} band is not known.

Two of the compounds studied, aniline hydrobromide and benzidine dihydrochloride, were not included in Table V because they do not have significant absorption in this region.

The assignments in the above discussion indicate that the charged nitrogen atom tends to increase the frequency of the hydrogen deformations on the adjacent atoms. The shift, however, does not appear to be very great and the asymmetric methyl deformation and the methylene deformation usually appear in the expected range, although at the upper end of the range. The symmetric methyl deformation is apparently shifted about 20 cm^{-1} upwards.

Although the number of compounds studied is small, this study indicates that the NH^+ group absorbs at about 1435 cm^{-1} in alkyl substituted ammonium salts.

TABLE V

THE SPECTRAL BANDS OF SOME MONOSUBSTITUTED AMMONIUM COMPOUNDS IN THE 1490-1350 cm^{-1} REGION

Compound	Frequency in cm^{-1} (a)		
$\text{CH}_3\text{NH}_3\text{Br}$			1409s
$\text{C}_2\text{H}_5\text{NH}_3\text{Br}$	1473s	1466s	1397m 1364w
$\text{C}_3\text{H}_7\text{NH}_3\text{Br}$		1467m 1463m	1399m
$(\text{CH}_3)_2\text{CHNH}_3\text{Br}$	1474m		1400m 1384m
$\text{C}_4\text{H}_9\text{NH}_3\text{Br}$		1467m	1400w 1381w
$\text{BrCH}_2\text{CH}_2\text{NH}_3\text{Br}$	1485m		1427m
$\text{HOCH}_2\text{CH}_2\text{NH}_3\text{Br}$	1478m	1458m	
$(\text{CH}_3\text{NH}_3\text{Br})_2$			1351m
HONH_3Br	1477s	1460s	
$\text{H}_2\text{NCONHNH}_3\text{Cl}$		1447m	1385m
$\text{C}_6\text{H}_5\text{NHNH}_3\text{Cl}$		1449m	
$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3\text{Br}$	1475s	1466s 1456s	1385s
$\text{C}_{10}\text{H}_7\text{NH}_3\text{Br}$		1448m	1371m 1361m

(a) The letters w, m, and s which follow the frequency stand for the intensity of the band and represent weak, medium, and strong intensity respectively.

TABLE VI

THE SPECTRAL BANDS OF SOME POLYSUBSTITUTED AMMONIUM
COMPOUNDS IN THE 1600-1350 cm^{-1} REGION

Compound	Frequency in cm^{-1} (a)					
$(\text{CH}_3)_2\text{NH}_2\text{Br}$	1589m	1471s	1435w	1428w	1408m	
$(\text{C}_2\text{H}_5)_2\text{NH}_2\text{Br}$	1570w	1483s	1462m	1440m	1393m	1378w
$(\text{C}_3\text{H}_7)_2\text{NH}_2\text{Br}$	1584m	1475m	1461m	1453s	1416m	
$[(\text{CH}_3)_2\text{CH}]_2\text{NH}_2\text{Br}$	1582m	1470s	1444s	1421m	1403s	1386m
$(\text{CH}_2=\text{CHCH}_2)_2\text{NH}_2\text{Br}$	1581w	1464m	1437s			1380w
$(\text{CH}_3)_3\text{NHBBr}$		1478s		1430m	1403m	
$(\text{C}_2\text{H}_5)_3\text{NHBBr}$		1477m	1436m	1403m	1388w	1378w
$(\text{C}_3\text{H}_7)_3\text{NHBBr}$		1474s	1465s	1444m	1403m	1381m
$(\text{CH}_3)_4\text{NBr}$		1488s			1405m	1399m
$(\text{C}_2\text{H}_5)_4\text{NBr}$		1498s	1449s	1407s	1401s	1376s
$(\text{CH}_2=\text{CHCH}_2)_4\text{NBr}$		1464s		1426s		1371m

(a) The letters w, m, and s after the frequency stand for the intensity of the band and represent weak, medium, and strong intensity respectively.

CHAPTER IV

SUMMARY AND CONCLUSIONS

In this work, the infrared spectra of some substituted ammonium salts were studied in the 2-9.5 micron region. Most of the compounds were monosubstituted derivatives, but some di-, tri-, and tetra-substituted compounds were also included.

One of the purposes of this study was to determine where the N-H stretching and deformation vibrations occur in these types of compounds. It was found that when the adjacent carbon was saturated, the NH_3^+ asymmetric stretching vibration in the monosubstituted compounds occurred in the range $3077\text{-}3096\text{ cm}^{-1}$, while the symmetric vibration occurred in the range $3003\text{-}3046\text{ cm}^{-1}$. The only exception to this observation was ethyl ammonium bromide, which had a single band at 3049 cm^{-1} . This spectrum was rather poorly resolved, so it was not possible to determine whether or not this anomalous behavior was real or apparent. For the monosubstituted compounds, which contained a pair of mobile electrons on the adjacent atom, it was not possible

to determine with certainty whether the NH_3^+ stretches occurred in the ranges given above. In some cases, bands did appear in these ranges, but an unambiguous assignment was not possible. This type of compound also showed another difference from the compounds where the adjacent carbon was saturated. They all had a strong band in the $2706\text{--}2554\text{ cm}^{-1}$ region where the other type had only weak bands. It is possible that this strong band is due to one of the NH_3^+ stretching fundamentals.

The NH_3^+ asymmetric and symmetric deformations were assigned the ranges $1599\text{--}1569\text{ cm}^{-1}$ and $1505\text{--}1492\text{ cm}^{-1}$ respectively. A possible exception to these ranges may occur when the NH_3^+ group is attached to an aromatic ring. In the three compounds of this type which were studied, it was not possible to assign a definite pair of bands to these vibrations, since these compounds also have other bands in this region. The ranges given above agree very well with the ranges quoted by Randall⁽⁷⁾ for amino acid hydrochlorides. The symmetric NH_3^+ deformation appears, in most cases, to be stronger and more stable in position than the asymmetric deformation. The behavior has also been noted for the symmetric methyl deformation as compared to the asymmetric deformation.⁽¹⁴⁾

All of the monosubstituted compounds had bands in the range $2800\text{--}2350\text{ cm}^{-1}$ which were assigned to some type of NH_3^+ vibration. However, most of these bands, except for the ones mentioned above, were weak.

No definite ranges could be determined for the stretching vibrations of the NH_2^+ group. The spectra indicated, however, that these bands probably do not occur in the C-H stretching region, but are probably found below 2800 cm^{-1} . All of the disubstituted compounds studied had several strong bands in the $2800\text{--}2350\text{ cm}^{-1}$ region which probably arise from the NH_2^+ fundamentals, but the position and number of these bands varied too greatly for any definite assignments to be made. The expected NH_2^+ deformation vibration, however, was identified with a band in the range $1589\text{--}1570\text{ cm}^{-1}$.

It was not possible to assign any bands to the expected NH^+ stretching vibration. The spectra indicate that this band probably occurs in the $2800\text{--}2350\text{ cm}^{-1}$ region. All of the trisubstituted compounds studied had several strong bands in this region, but their positions and number varied widely. The NH^+ deformation vibration was tentatively identified with a band in the range $1444\text{--}1430\text{ cm}^{-1}$. The relatively great intensity of this band as compared to that of the CH group was explained by the

fact that the positive charge on the nitrogen would lead to a large change in dipole moment in the vibration.

It was noted that the stretching vibrations of the NH_3^+ group occur at a higher frequency than those of the NH_2^+ group, which in turn are a little higher than that of the NH^+ group. This same trend has been noted for the methyl, methylene, and tertiary CH groups. The N-H groups and their carbon analogues also appear to follow the same trend with respect to the deformation vibrations. The asymmetric XH_3 and the XH_2 deformations occur at about the same frequency, while the XH deformation occurs at a much lower frequency.

This study indicates that it should be possible to determine the degree of substitution of a substituted ammonium salt by an examination of the $3100\text{-}3000\text{ cm}^{-1}$, $2800\text{-}2350\text{ cm}^{-1}$, and $1600\text{-}1500\text{ cm}^{-1}$ regions. Monosubstituted salts have relatively strong bands in the first and third region. Disubstituted salts have relatively strong bands in the second and third regions. Trisubstituted salts have relatively strong bands in the second region only. Tetra-substituted salts have no significant absorptions in any of these regions. These correlations would apply only to compounds in which the substituting groups themselves have no absorptions in these regions. The presence of aromatic rings, for example, would greatly complicate the identification.

Edsall⁽⁶⁾ noted a methyl stretch at about 3030 cm^{-1} in the Raman spectra of methyl substituted ammonium salts. This band was found to occur also in the infrared. No other definite information could be found for the direction or degree of shift of adjacent hydrogen stretches. Shifts in both directions were indicated, but no correlations of the shifts with structure could be made. In the case of hydrogen deformations on adjacent carbon atoms, it was found that the adjacent charged nitrogen atom always shifted the deformation to a higher frequency. The shift was usually about 20 cm^{-1} .

Tentative assignments were made for most of the bands appearing above 1350 cm^{-1} . No attempt was made to assign the bands which occurred below this frequency.

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BIOGRAPHICAL NOTES

Robert S. Silas was born on May 5, 1930, in Miami, Florida, and received all of his early schooling in the public schools of that city. He graduated from Miami Senior High School in June, 1947.

In September, 1947, he entered the University of Florida, from which he received the degree Bachelor of Science in Chemistry with High Honors in June, 1951. He immediately entered the Graduate School of the University of Florida where he was employed as a graduate assistant for some time. He was awarded a National Science Foundation Pre-doctoral Fellowship for 1952-53 and again for 1954-55. He is a member of Phi Beta Kappa, Phi Kappa Phi, Phi Eta Sigma, Gamma Sigma Epsilon, Delta Phi Alpha, and Kappa Kappa Psi, honorary fraternities, and of Alpha Chi Sigma, the professional chemical fraternity.

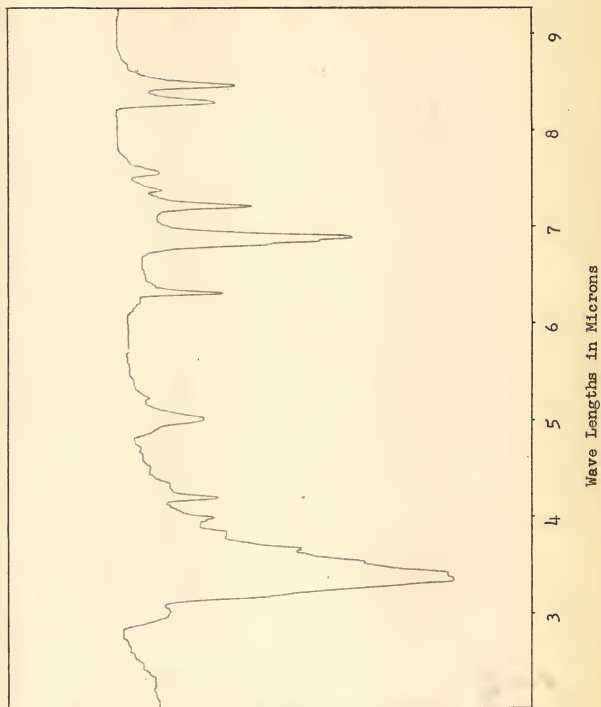
APPENDIX

Spectrum of
Methyl Ammonium Bromide

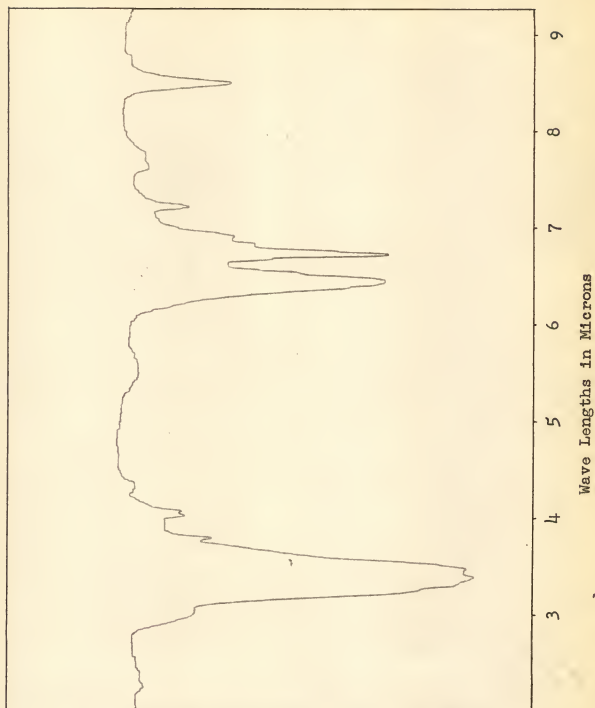
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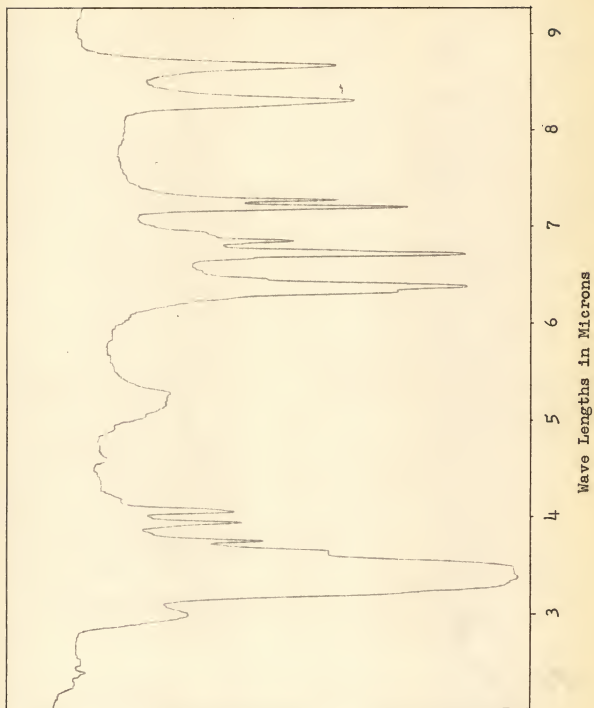
Spectrum of Ethyl Ammonium Bromide



Spectrum of Propyl Ammonium Bromide



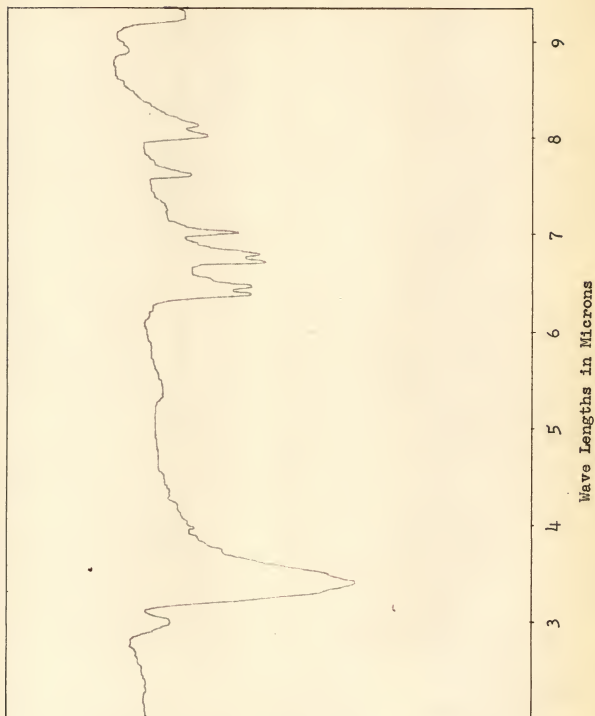
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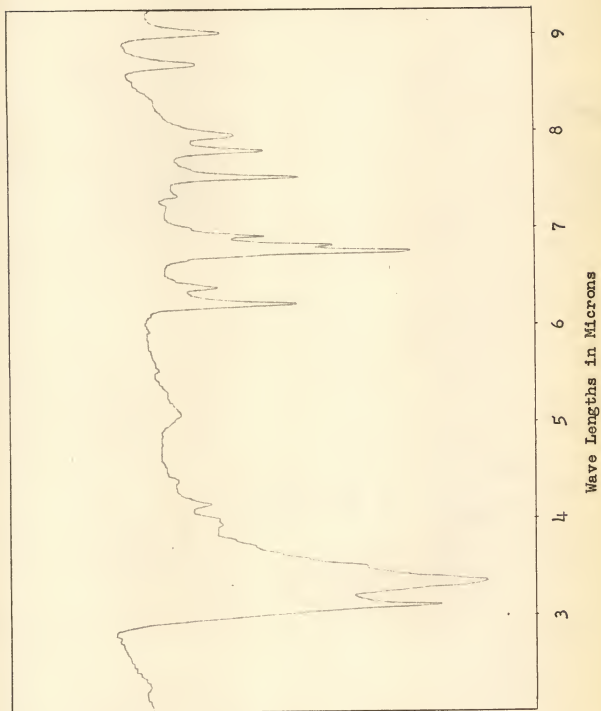
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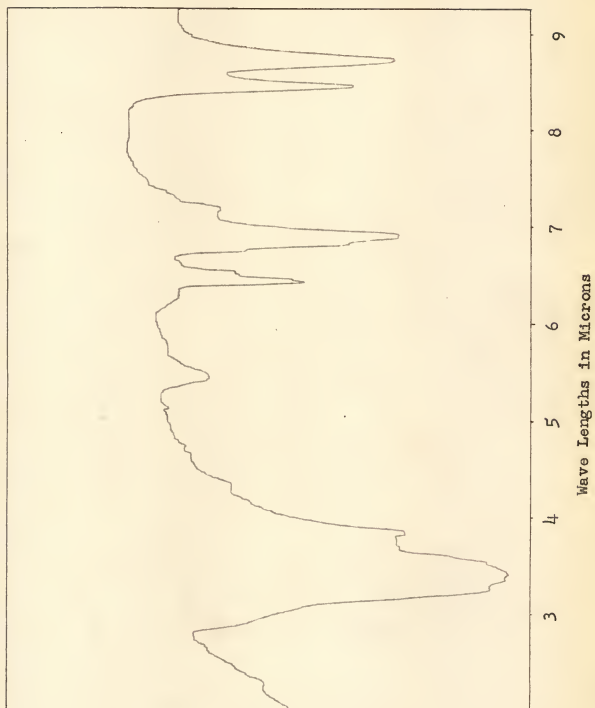
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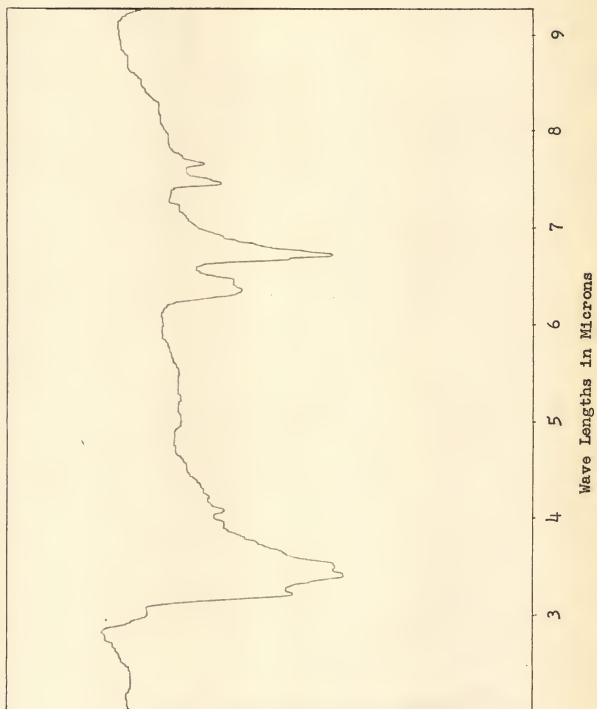
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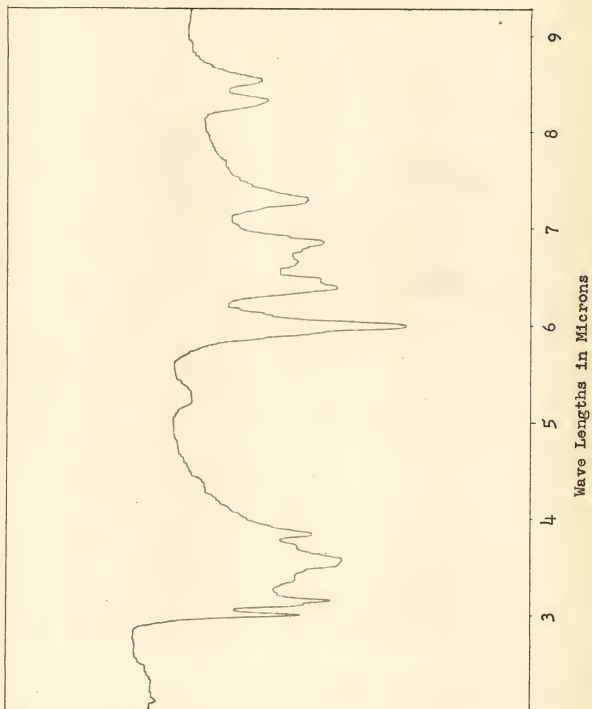
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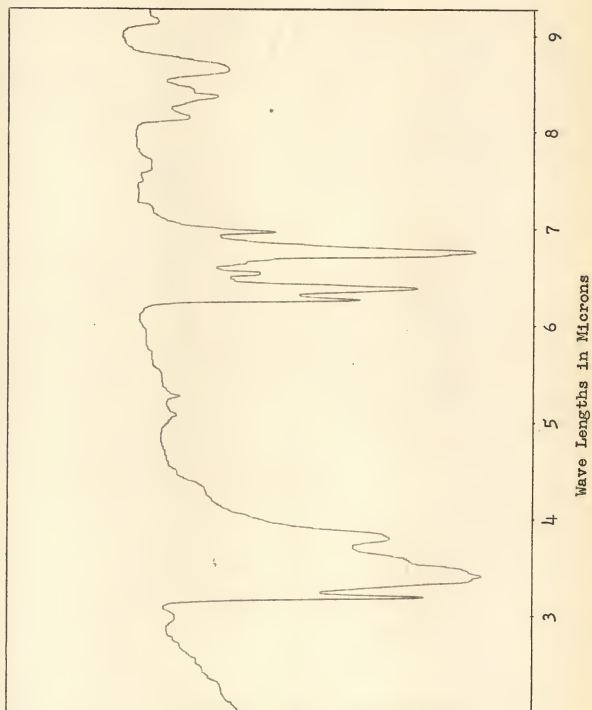
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Ethylene Diammonium Bromide



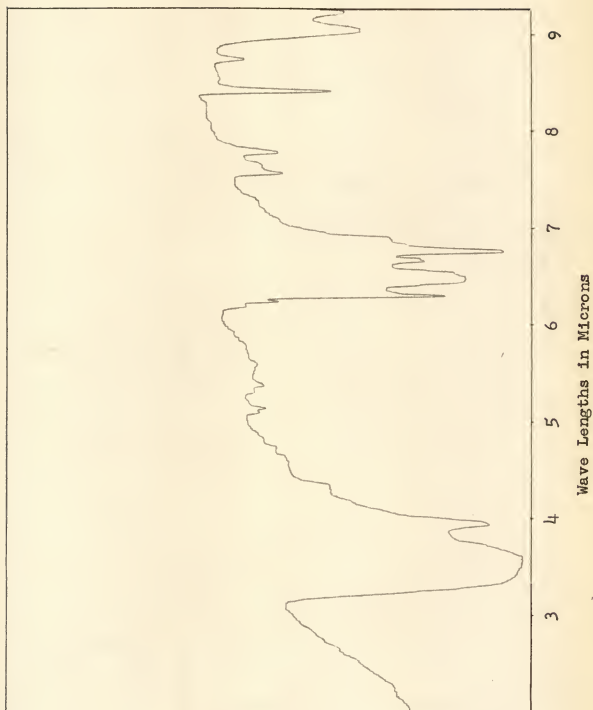
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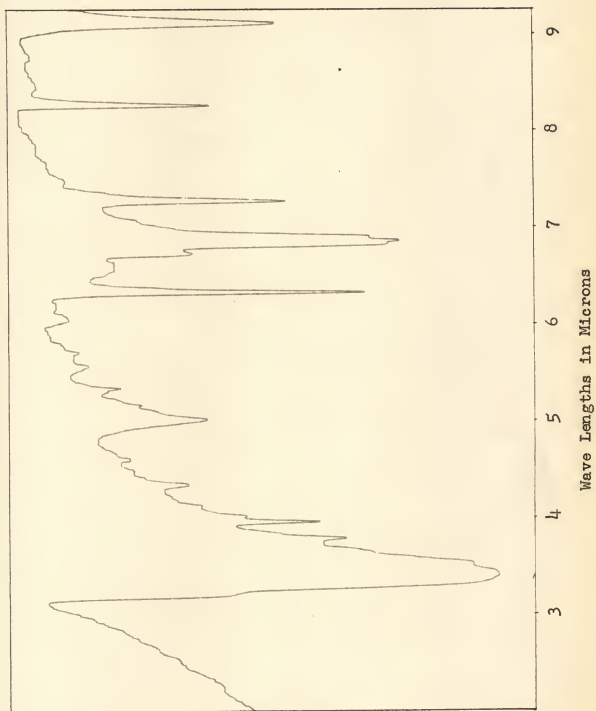
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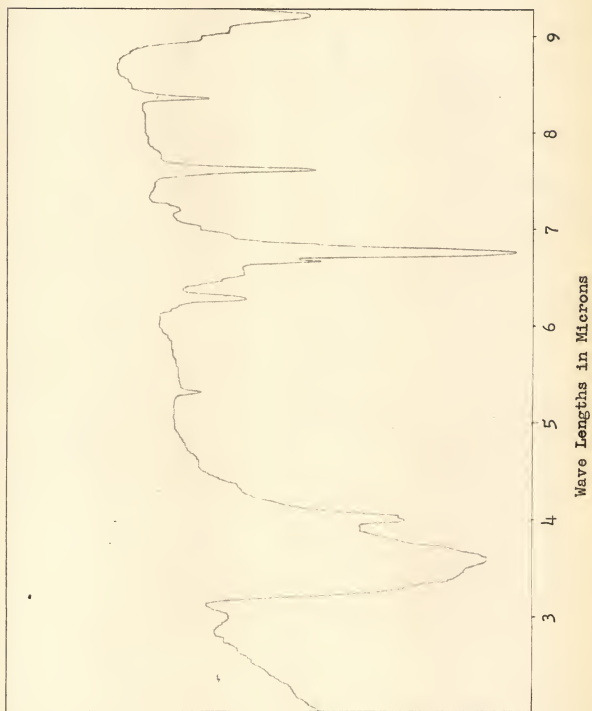
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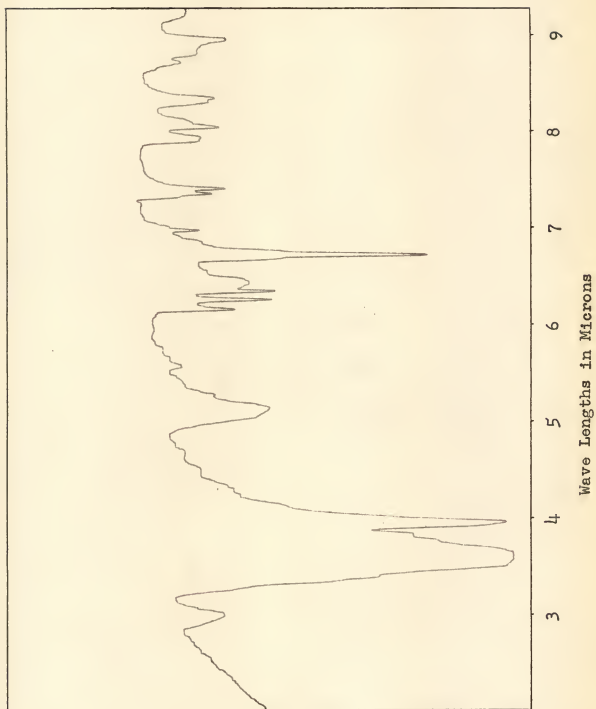


Spectrum of Benzyl Ammonium Bromide

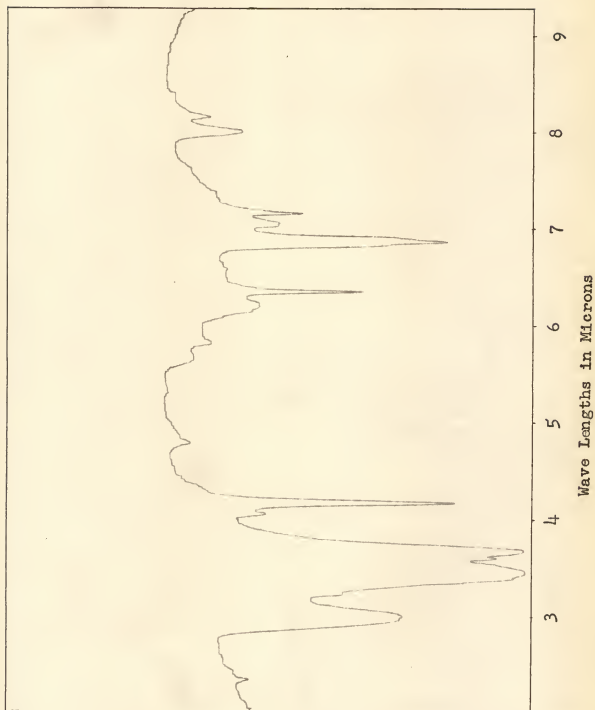


Spectrum of Benzidene Dihydrochloride

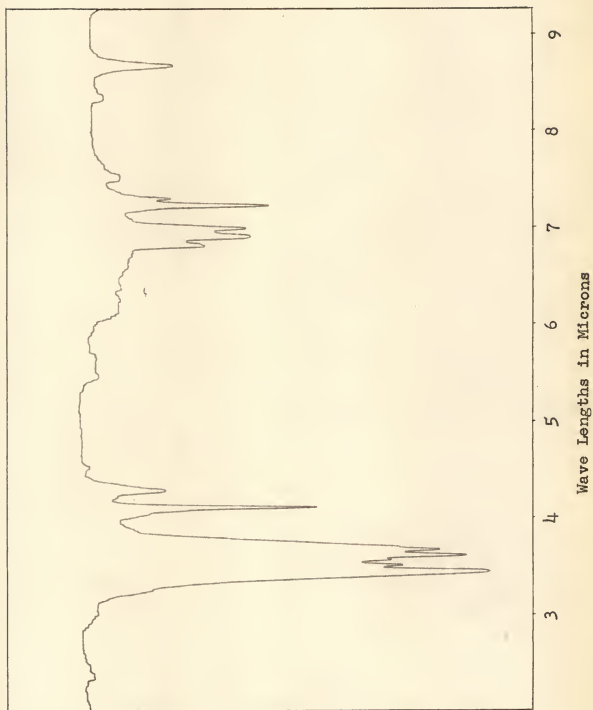


Spectrum of α -naphthylammonium Bromide

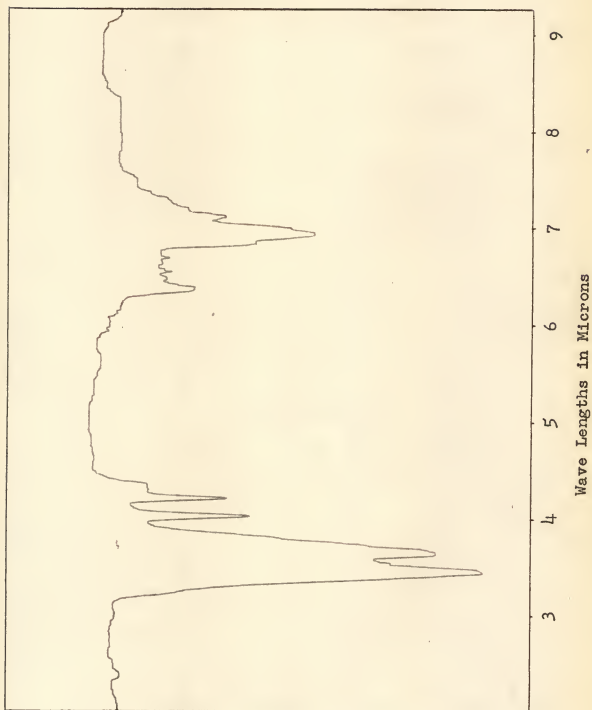
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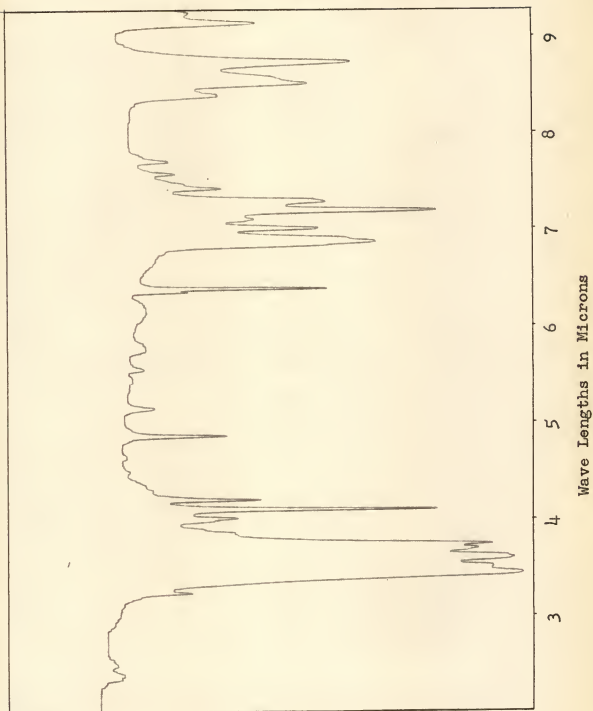
Spectrum of Diethyl Ammonium Bromide



Spectrum of Dipropyl Ammonium Bromide



Spectrum of Diisopropyl Ammonium Bromide



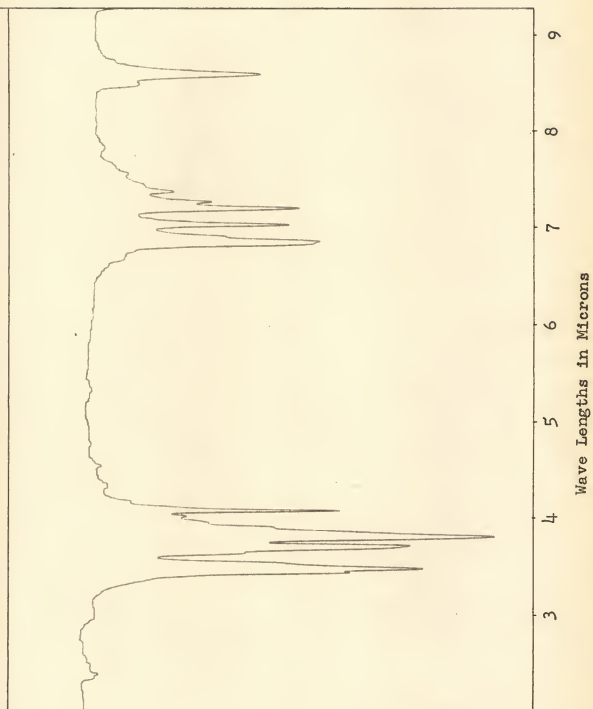
Spectrum of Diallyl Ammonium Bromide



Spectrum of Trimethyl Ammonium Bromide



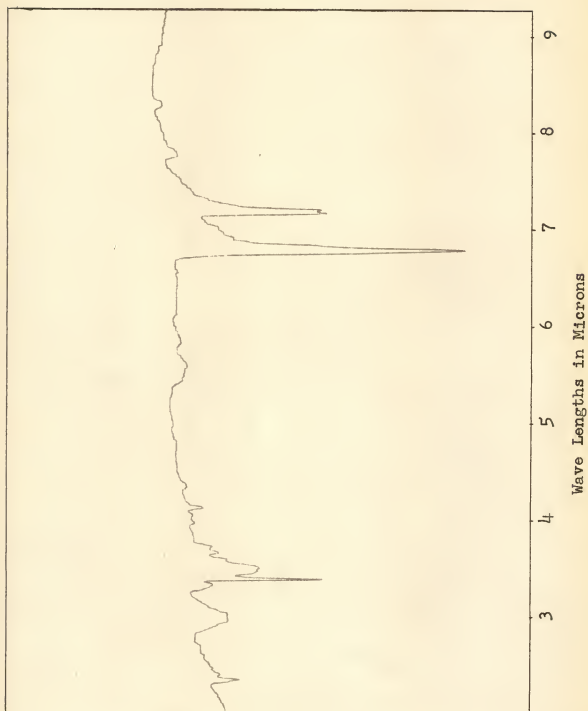
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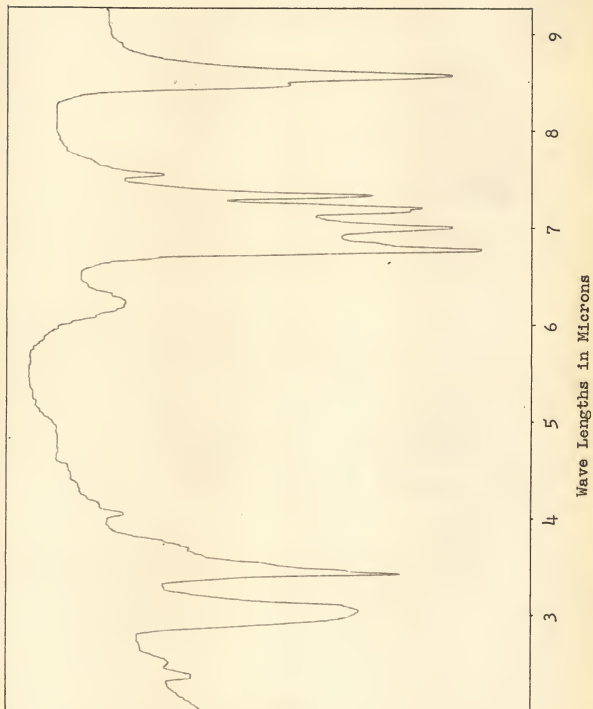
Spectrum of Tripropyl Ammonium Bromide



Spectrum of Tetramethyl Ammonium Bromide



Spectrum of Tetraethyl Ammonium Bromide



Spectrum of Tetraallyl Ammonium Bromide

